Extraction of Oil from Tannery Fleshings for Chamois Leather Tanning

PERIS N. WAINAINA, PAUL TANUI and BENSON ONGARORA*

Department of Chemistry, Dedan Kimathi University of Technology, Private Bag, Dedan Kimathi – Nyeri, Kenya

Abstract

The process of leather manufacturing produces vast amounts of solid waste annually (8.5 million tons worldwide), and most of the solid waste (80%) is produced in pre-tanning operations. The fleshing operation to remove flesh, subcutaneous tissue and natural fat from the flesh side of hide/skin (fleshings) accounts for 50-60% of total solid waste. Attempts to extract oil from the fleshings have been made, however, the application of the oils from fleshings in tanning has not been explored. The oil tanning process takes about 12 days (compared to chrome tanning which takes approximately 6 hours), and this explains why the technology is not commonly used. The objective of the research was to discover whether the fleshing oil could be used for chamois leather tanning.

The oil was extracted from goat fleshings and characterised using Soxhlet extraction and chemical methods. The fat content, iodine value, acid value, percentage free fatty acid and saponification value of green fleshings were 27.56 ± 0.40%, 73.79 ± 0.34, 7.38 ± 0.13mg/g, 3.71 ± 0.06 and 187.08 ± 0.22 mg/g respectively while that of limed fleshings was 17.48 ± 0.55%, 67.40 ± 0.35, 6.08 ± 0.02mg/g, 3.06 ± 0.06 and 184.66 ± 0.33mg/g respectively. The results of the study show that the physical and organoleptic properties of fleshing oil-tanned leather were similar to those of cod oil-tanned leather. Tensile strength, elongation, tear strength and water absorption of the chamois leather were 27.88 ± 0.07N/mm^2, 55.75 ± 0.17%, 56.64 ± 0.29N/mm, 211% respectively. The physical and organoleptic properties of the leathers resulting from this study suited the requirements for chamois leather.

INTRODUCTION

Most of the solid waste (80%) in leather manufacture[1] is produced in pre-tanning operations.[2] Fleshings are estimated to be (50-60)% of total solid wastes,[3] these consist of proteins, natural fats, and other constituents with a high potential use. Unfortunately, this waste does finds little usage and are currently disposed in dumping sites with a negative effect on the environment.

Fleshing waste has a high amount of (4-18) % fat,[4] which could be a great source for manufacture of an oil tanning agent. Fleshings are used for the production of adhesives, gelatin, fatliquors and biodiesel[5] but attempts to use the oil as a tanning agent have not been made. Oil tanning involves the impregnation of the skin with oil in fulling stocks allowing oxidation of oil, with the products of the reaction having a tanning action. The oxidation process was done by hanging the tanned material in a warm stove for about 10-12 days. However, in the present study, the leather was pretanned using glutaraldehyde then tanned using fleshing oil and then oxidised using hydrogen peroxide, this method of tanning reduces the long oxidation period.[6]

Unsaturated free fatty acids in the oil combine with oxygen to form oxidised fatty acids, aldehydes and peroxides which effect the tanning action on the pelt. The actual nature of the tannage is not known except for the following observations; the unsaturation of the oil decreases as the process progress, peroxy derivatives are formed, hydroxyl function appears and acrolein is produced.[7] The tannage is an aldehydic reaction since the procedure is characterised by the release of acrolein, and polymerisation of the oil, the availability of the latter could represent the difference between the qualities of oil- and aldehyde-tanned leathers. The acrolein delivered by the oil tannage reaction could be utilised for an item like aldehyde-tanned calfskin. However it is, by implication as a part of wood smoke, harmful.[8] Chamois leather is best known for properties of holding water, cleaning and drying washed surfaces. This use of oil tannage imparted softness, stretchability, washability and increased the thickness of the leather. The thickness increased to a reasonable degree due to shrinkage effect of oil tannage. This chamois leather meets the global demand for washable leather which is highly valued. The leather processed from this non-conventional source is suitable for manufacturing of fancy small leather goods.

MATERIAL AND METHODS

Sample preparation

Goat fleshings were collected from Sagana tannery. The limed fleshings were washed with water, delimed with ammonium sulphate. The fleshings were cut into small pieces and sun dried.

Extraction of oil

The Soxhlet method was employed for the extraction of oil from the fleshings. 10g of the dried fleshing sample was placed in a thimble inside the Soxhlet extractor and the sample was then refluxed for

* Corresponding author: E-mail: benson.ongarora@dkut.ac.ke

approximately 8 hours with petroleum ether (80-100C B.Pt.). The entire extraction was carried out according to a procedure described in literature.[9]

For large scale oil production, an extractive boiler equipped with a heating stove will be more appropriate. Upon washing of the limed fleshing waste using water, the waste will be charged into the extractive boiler and heated to the prescribed temperature of about 80°C.[10] The mixture will not require agitation since agitation at higher temperatures leads to degradation the oil (high acidity index) despite the significant gain in the recovery of fatty material that comes with agitation.[13] If large quantities of fleshing waste are involved, the extracted oil may be left to stand in settling tanks to allow for separation (from aqueous medium) and subsequent separation by draining into storage tanks. On the other hand, this study used the extracted oil without further purification. However, the majority of marketable oils and fats are subjected to purification processes in order to improve smell and appearance; remove colloidal particles, colouring and volatile substances, and moisture among other contaminants.[14]

Oil analysis

The total fat content of goat fleshing was determined using Association of Official Analytical Chemists (AOAC), 2005 method. Iodine value was analysed using Wijs method.[11] Acid value was measured using AOAC method. Free fatty acid content was determined by converting acid value to free fatty acid content.[10] Saponification value was also measured also using an AOAC method.

Tannage

The goatskins were thoroughly washed using 400% water and 0.5% wetting agent. Liming was done with 200% water and 8% lime (in two instalments) for 24 hours and hand hauling was done every 15 minutes for two hours. The tanning drum was drained and the limed pelt was washed with clean water. Deliming: 150% water at normal temperature, 2% ammonium sulphate and 1% sodium metabisulphate were added and the drum run for one hour. The cross section was checked by phenolphthalein (colourless). The delimed pelts were then bated with 1% enzymatic bate for one hour. Table I shows the procedure of tanning using fleshing oil. The leather was hooked to dry, toggled then snuffed and dedusted.

Leather analysis

The leather was conditioned using ISO 2419. Physical properties,[12] water absorption, tear strength, tensile strength, and elongation at break, were measured using IUP methods. Organoleptic properties, *i.e.* softness, colour and odour, were tested by two chamois leather experts.

RESULTS AND DISCUSSION

Determination of oil content and yield

The oil content of green (G) and limed (L) fleshings from goatskins were determined and tabulated in Table II. Petroleum ether was used as the solvent for oil extraction. It was observed that the green fleshing from goatskin had the maximum oil content of 27.56 ± 0.40 % while limed fleshing oil had lower oil content of 17.48 ± 0.55%. Animals contain 5-30% fat content suggesting that the fleshing oil falls in the range of literature values.[13] It is obvious that during liming, the fat is saponified and hence lowers the fat content in the limed fleshings. Green fleshings, which are devoid of any chemicals would be material for preparation of a product of higher quality. However, most tanneries carry out only limed fleshing. Hence, it becomes

TABLE I
Procedure of tanning using fleshing oil

Process	Chemicals	Amount (%)	Time (h)	Remarks
Pickling	Water	150	2	The pH was adjusted to 3.2
	Salt	10		
	Formic acid	0.8		
	Sulphuric acid	1		
Pre-tanning	Glutaraldehyde	0.5	2	The pH was adjusted to 8.5 and the skins were piled for 12 hours
Oil tanning	Fleshing oil or	30	6	The skin was uniformly drummed along with oil for 6 hours
	Cod oil (control)			
	Hydrogen peroxide (100 vol)	6	4	The skin was drummed for 6 hours
(inside the drum)				
Oxidation (outside the drum)			12	The materials were hanged on the toggle drier at room temperature
Alkali wash	Water	400	1	The leather was washed three times and drained.
	Soda ash	0.25		
	Wetting agent	0.5		
The leather was hooked to dry, toggled then snuffed and dedusted.				

necessary to clean the limed fleshings free of chemicals, so that a quality product can be obtained. Both oils showed similar colours.

TABLE II
Chemical properties of extracted oil from goat fleshings

Characteristics	Source of oil	
	GGF	GLF
Fat content (%)	27.56 ± 0.40	17.48 ± 0.55
Acid value	7.38 ± 0.13	6.08 ± 0.02
Free fatty acid (%)	3.71 ± 0.06	3.06 ± 0.01
Saponification value	187.08 ± 0.22	184.66 ± 0.33
Iodine value	73.79 ± 0.34	67.40 ± 0.35

Saponification value

Saponification value of oil is a measure of the average molecular weight of the triacylglycerol in a sample. The smaller the saponification numbers the larger the average molecular weight of the triacylglycerol present *i.e.* saponification value is inversely proportional to the mean molecular weight of fatty acids.[11] The saponification value of green (GGF) and limed (GLF) oils extracted from goat fleshings were as shown in Table II. The saponification value of green fleshing GGFaverage was187.08± 0.22mg/g, limed fleshing GLFaverage was 184.66± 0.33mg/g which is in good agreement with the reported works.[10] All results fall within the standard value that is 184-192.[15] Oils having saponification values 'between' 180-233 have smaller molecules and so their penetration powers into the leather should be greater, this in turn will improve the softness of the final leather.

Acid value

Acid value of the oils from green and limed fleshings were measured and the values are shown in Table II. Acid value is a measure of rancidity. If the values are high, the fat or oil will become more rancid and *vice versa*. The acid value of oil used for tanning should be below 8.0mg/g.[16] The average acid value for the oil extracted from green fleshings is 7.38 ± 0.13mg/g and that of limed fleshings is 6.08 ± 0.02mg/g, both being less than 8.0mg/g. The percentage free fatty acid (FFA) can be calculated based on acid value. The following formulae was used and the values are given in Table II.

$$FFA = AV \times 0.503$$

Iodine value

The main characteristic of oil from fleshing waste that is required for tanning is the iodine value. The iodine value (IV) gives a measure of the average degree of unsaturation of a lipid: the higher the iodine value, the greater the number of C=C double bonds.[11] Table II shows the determined iodine value of fleshing oil. A low iodine number shows that the fat has a low quantity of unsaturated fatty acid,[11] all the samples showed low iodine values. Fats and oils are usually classified on the basis of their iodine value as drying oil 125-181; semi-drying oil 85-128 and non-drying 8-129.[17] All of our results fall in the range 67-74. Hence, they can be called non- drying oils and will thus require more time for tanning than the one with high iodine value. The chemical properties of the extracted fleshing oil are summarised in Table II.

Comparison of the fleshing oil and cod oil chemical properties are given in Table III.

TABLE III
Chemical properties of fleshing oil and cod oil

No.	Chemical properties	Fleshing oil	Cod oil
1	Acid value	6 – 8	10 – 13
2	Fatty acid content (%)	3 – 4	5 – 6
3	Saponification value	185 – 187	199 – 204
4	Iodine value	66 – 75	80 – 120

Tanning assessment

The leathers obtained had similar properties except for colour where the fleshing oil leathers were yellow, the one that was tanned using cod oil had an undesirable dark colour attributed to the rapid oxidisability of cod oil due to high iodine value.[7] The leathers wet back immediately when immersed in water and absorbed large amounts of water – the water uptake of chamois leather is 600% on dry weight, the hydrophilic property may be associated with hydroxyl groups of oil-tanned residues.[7] The leather showed the unique Eward effect of chamois, whereby; when immersed in hot water at about 70°C, it shrank immediately and thickened, when the shrunken leather was immersed in cold water it relaxed immediately and regained 90% of its original area, this test confirmed that tanning was effective.[19]

TABLE IV
Physical properties of chamois leather

Physical properties	Chamois leather		
	Fleshing oil	Cod oil	Standard value (minimum)
Thickness (mm)	1.39 ± 0.13	1.42 ± 0.19	0.3-1.5
Tensile strength (N/mm^2)	27.88 ± 0.07	29.64 ± 0.86	>7.5
Elongation at break (%)	55.75 ± 0.17	58.63 ± 1.24	>50
Tearing strength (N/mm)	56.64 ± 0.29	58.01 ± 0.51	>15
Water absorption (%) in 2 hours	211	357	>100

Physical properties

Fleshing oil-tanned leather had similar properties to those of cod oil-tanned leather. The leather fulfilled the SNI-06-1752-1990 standard for chamois leather.[18] Both oil-tanned leathers met the quality standard. The physical properties of both leathers are shown in Table IV which shows that skins tanned with fleshing oil gave properties close to those of cod oil-tanned leather.

Organoleptic properties

The softness of chamois leathers from fleshing oil and cod oil were similar.[18] The colour of fleshing oil-tanned leather was brighter than that of cod oil-tanned leather.[7] Fleshing oil-tanned leather has better odour than cod oil-tanned leather. Organoleptic properties of both leathers are shown in Table V.

TABLE V
Organoleptic properties of fleshing oil- and cod oil-tanned leather

Organoleptic properties	Fleshing oil-tanned leather	Cod oil-tanned leather
Softness	7 – 8	7 – 8
Colour	8 – 9	7 – 8
Odour	7 – 8	4 – 6

On a 10-point scale, 0 = poor, 10 = excellent.
The result was average results.

CONCLUSION

This study shows that fleshing oil could find an application in processing chamois type leather. Physical and organoleptic properties of fleshing oil-tanned leather were similar to those of cod oil-tanned leather. All of the parameters fulfilled the quality standard required. The present study has dual benefit to the tanner, that is it allows production of a valuable product for commercial use and also reduces the environmental impact.

ACKNOWLEDGEMENT

We would like to acknowledge the African Development Bank and Dedan Kimathi University of Technology for funding and technical support.

(Received January 2019,
revised March 2019)

References

1. Kowaiska, M. and Zbikowska, A., pH as a parameter for the exponential stability of fatliquor emulsions. *J. Soc. Leather Technol. Chem.,* 2014, **98**, 23.
2. Çolak, S., Zengin, G., Özgünay, H. *et al.,* Utilization of leather industry pre-fleshings in biodiesel production. *J. Amer. Leather Chem. Ass.,* 2005, **100**, 137.
3. Kanagaraj, J., Velappan, K. C., Babu, N. K. C. *et al.,* Solid wastes generation in the leather industry and its utilization for cleaner environment. *J. Sci. Ind. Res*., 2006, **65**, 541.
4. Lupo, R., Planning and realization of an innovative plant for the treatment of the by product 'fleshing', with increment of its utilization. *DELTACQUE Srl – Technical* report. 2004.
5. Nasr, A. I., Reusing limed fleshing wastes as a fatliquor In leather processing. Egypt. *J. Chem.,* 2017, **60**, 919.
6. Suparno, O., Sa, E. G., Kartika, I. A. *et al.,* Chamois leather tanning accelerated by oxidizing agent. *Jurnal Teknik Kimia Indonesia,* 2015, **11**, 9.
7. Sharphouse, J., Theory and practice of modern chamois leather production. *J. Soc. Leather Technol. Chem.,* 1985, **69**, 29.
8. Laughlin, M., Aldehyde Tanning – A Historical Article on Leather Production, 2011.
9. Hashem, A. and Nur-a-tomal, S. One step to prepare fatliquor from the extracted fat of cowhide fleshings for using in leather processing. IULTCS, (2015), 1-6.
10. Getahun, E. and Gabiyye, N. Experimental investigation and characterization of biodiesel production from leather industry fleshing wastes. *Int'l. Journal of Renewable and Sustainable Energy*, 2013, **2**, 120.
11. Odoom, W. and Edusei, V. O., Evaluation of saponification value, iodine value and insoluble impurities in coconut oils from Jomoro District in the Western Region of Ghana. *Asian Journal of Agriculture and Food Sciences*, 2015, **03**, 2321.
12. Suparno, O. N. O. and Kartika, I. K. A. A. Chamois leather tanning using rubber seed oil. *J. Soc. Leather Technol. Chem.,* 2000, **93**, 6.
13. Priebe, G. P. S. and Gutterres M., Olein production from pre-fleshing residues of hides in tanneries. *Lat. Am. Appl. Res.,* 2012, **1**, 42.
14. List, Gary, R., and Patterson, H. B. W., Bleaching and Purifying Fats and Oils: Theory and Practice. Urbana, Ill: AOCS Press,(2009).
15. Kassahun, W., Preparation of leather fatliquor *cum* filler from fleshing waste for retanning process in leather manufacture. Addis Ababa University, 2014.
16. Eiri, Handbook of Leather and Leather Products Technology. Delhi: Engineers India Research Institute, (2006).
17. Duel, H. J., The lipids: their chemistry and biochemistry. New York Inter Science Publishers, (1951), Ch.1, 53.
18. Badan Standarisasi Nasional. National Standard for Chamois Leather. In SNI 06-1752-1990, Jakarta.
19. Covington, A., *Tanning Chemistry: The Science of Leather*. Cambridge, UK: (2009). Royal Society of Chemistry.